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SURVEY OF RECENT RESEARCH ON FLAME EXTINGUISHMENT December 1962

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### FOREWORD

This report was prepared under Contract Nr. AF 33(657)-7617, "A Research Program for Understanding the Mechanisms of Flame Inhibition." The contract was initiated under Project Nr. 6075, Task Nr. 607505, by the Flight Accessories Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio with Mr. B. P. Botteri as project engineer.

The report covers literature appearing between May 1961 and September 1962, and was prepared at the Dayton Laboratory of Monsanto Research Corporation. An earlier survey was published as ASD Technical Report 61-408. Dr. G. B. Skinner was project leader. The assistance of Mrs. F. K. Finke is gratefully acknowledged.

### ABSTRACT

Current state-of-the-art in flame extinguishment by chemical and physical agents is reviewed, based on papers published during the period April 1961 - August 1962, in technical journals, trade literature and Government reports. Papers presented in two symposia are also considered: an American Chemical Society Symposium on Fire Control Research, held at the September 1961 meeting of the Society, and the Ninth Symposium on Combustion, August, 1962.

The survey brings up to date an earlier survey published as ASD TR 61-408.

#### PUBLICATION REVIEW

This report has been reviewed and is approved.

For the Commander:

William C Savage
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## SURVEY OF RECENT RESEARCH ON FLAME EXTINGUISHMENT

### 1. INTRODUCTION

This survey reviews the current state of knowledge of flame extinguishment by both chemical and physical agents. A series of survey reports (Ref. 32) covers the subject to the beginning of 1959, while a report from our laboratory in 1961 (Ref. 70) critically reviews progress in chemical flame extinguishment from 1959 through April, 1961.

This report, then, deals with research on chemical agents during the past year, and on physical agents during the past three years. The literature, including journal articles and Government reports, has been covered up to August 1962.

Two meetings of importance in fire research were held in 1962. One was a four-week study of fire problems held at Woods Hole, Mass., 17 July - 11 August 1961.

The thirty participants, experts in various aspects of fire protection, recommended that within the Federal Government a fire group be established to collect and disseminate information on, and encourage the use of, new and improved methods of fire-fighting, and to support fire research. The report of the study group has been published (Ref. 64).

A symposium on fire control research was sponsored by the Division of Fuel Chemistry at the American Chemical Society meeting in Chicago, Sept. 3-8, 1961. The subjects considered ranged from fundamental studies on flame inhibition to studies on the most effective ways to use water and the protection of structures by fireresistant paint.

Also during the past year, the proceedings of the Eighth Combustion Symposium (Ref. 19) were published in full, and the Ninth Symposium was held. Of the many important papers presented at both meetings, only a handful dealt directly with flame extinguishment.

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### UNINHIBITED FLAMES

Pertinent fundamental research on uninhibited flames is reviewed here, because knowledge of uninhibited flames provides a foundation for our understanding of inhibition or extinguishment.

## 2.1 Progress in Flame Theory

Because of the physical and chemical complexity of flames, development of flame theory remains a difficult task. Recent publications have dealt chiefly with premixed laminar flames, for which the theoretical treatments are most advanced.

After several years of productive effort, Hirschfelder and Curtiss have discontinued their flame studies. A historical review of their work was given at the Ninth Combustion Symposium (Ref. 42). During the past several years, they succeeded in formulating in complete general terms the premixed flame equations. They were able to calculate temperature and composition profiles for several artificial reaction mechanisms, but were unable to solve the equations for any real flame, because of mathematical complexities. It seems likely, though, that the basic equations will be used by other workers and that solutions will eventually be obtained for flames such as  $\rm H_2-Br_2$ ,  $\rm H_2-O_2$  and  $\rm CH_4-O_2$ .

The somewhat less complete formulations of the premixed flame equations, previously reported by Lovachev, Spalding and Van Tiggelen, are being improved and applied. The development of their equations started with the very simple assumption that all flame reactions are negligibly slow below and very fast above an "ignition temperature", which lies between room temperature and the final flame temperature. The flame propagates as fast as cold gas can be brought up to the ignition temperature by heat conducted from the hot burned gases. The flame speed, therefore, is governed chiefly by the heat of reaction, the ignition temperature, and the thermal conductivity.

From this beginning, the flame equation has been modified and made more realistic by including the effects of diffusion of gases through the flame, and of reaction rates which are not simply step functions of temperature.

Several recent papers (Ref. 2, 44, 50, 51, 52, 53, 54, 55, 60, 78, 80, 82, 87) deal with the behavior expected in flames propagated by free radicals. Here the temperature dependence of the over-all reaction rate is neither a step function nor a simple exponential function. Rather it tends to lie somewhere in between. While complete calculations of flame properties from kinetic and transport properties are currently outside the scope of this method, it has been possible (Ref. 27, 28, 55) to relate the flame speed to the temperature profile of a flame rather exactly. Spalding and Vortmeyer (Ref. 73) have described a new analog computer which can be used to solve this type of flame equation.

This approximate flame theory has been used by Yang (Ref. 85) to develop relationships for extinction of flames either by reaching flammability limits or by quenching in tubes. In either case, quenching occurs when the rate of heat release by reaction is insufficient to keep the gas up to the ignition temperature, allowance being made for heat loss by conduction.

Only one reference (Ref. 49) to the theory of diffusion flames has been found. In it, A. Linan considers the rates of combustion reactions in the boundary layer between fuel and oxidizer, showing how reduction of the rate can lead to flame extinguishment.

The mechanism of ignition of a combustiole mixture, by a spark, for example, is discussed by Yang (Ref. 85). The minimum energy necessary for ignition is formulated in terms of heat loss from the sparked gas by conduction and radiation, and in terms of the chemical kinetics and heat of combustion. Both Yang and Thomas (Ref. 75) consider thermal ignition, in which reacting material is thermally insulated, so that the rate of reaction, being a function of temperature, is a function of the amount of reaction. Whether thermal ignition leading to an explosion occurs depends on the heat loss through the insulation, and eventually on whether the increase in reaction rate due to temperature rise exceeds the decrease in rate due to reactants being used up. These papers define the conditions leading to thermal ignition.

Flame theory is rapidly approaching the point where complete calculations can be made. On the one hand, high-speed computers are bringing the detailed calculations of Hirschfelder and Curtiss into the realm of possibility. On the other hand, "simplified" theories are being made more elaborate so that they are able to account more satisfactorily for experimental results.

## 2.2 Experimental Results

Much recent combustion research was reported at the Ninth Combustion Symposium in August, 1962. Lewis and Williams reported temperature, H2, O2, H2O, and calculated H profiles for a rich nitrogen-diluted  $H_2-O_2$  flame, the most complete set of data so far obtained for this flame system. Fristrom described his continuing efforts to measure radical as well as molecule profiles in lean methane-air flames, using small quartz probes in which the withdrawn gas samples are quickly mixed with another substance to convert radicals to characteristic stable compounds. Fenimore and Jones presented concentration profiles for hydrogen-air flames containing small amounts of hydrocarbons. These authors tabulated what are, in their opinions, the best values of a number of kinetic constants important in hydrogen and hydrocarbon flames. Kaufman also reported on several reactions of OH radicals which are important in combustion. These papers and others on fundamental flame processes were preprinted in full (Ref. 9), as were a number of papers on detonations (Ref. 83), whereas only abstracts of the other Symposium papers have been printed so far.

# 3. CHEMICAL FLAME INHIBITION

The consensus of previous research is that chemical inhibitors act by removing the relatively small number of active species (atoms and radicals) that propagate the flame. There is also some evidence that ions and electrons contribute to flame propagation and are removed by inhibitors. Recent studies leave these conclusions unchanged.

# 3.1 Inhibition by Hydrocarbons

Although hydrocarbons are themselves flammable, they inhibit the hydrogen-oxygen reaction by reacting with the H, O and OH radicals that propagate the reaction. R. R. Baldwin and co-workers have studied this phenomenon extensively using static bulb experiments, as reported in our earlier survey. They have recently reported new data on the inhibiting effects of methane and ethane, which in their earlier work were both found to inhibit, but in different ways.

They concluded (Ref. 11) that ethane inhibits by a "steady-state" process in which the ethane, by removing the free radicals, displaces the balance of chain branching and breaking reactions occurring in the gas mixture so that for a given hydrogen-oxygen composition and pressure, inhibited mixtures are unreactive to higher temperatures. In this case, the rate of reaction is either at an extremely slow rate (at lower temperatures) or extremely fast (at higher temperatures) with a sharp transition between the two.

On the other hand, when methane is added to a hydrogenoxygen mixture that would otherwise explode, the rate of reaction is reduced, but not so drastically as with ethane, so that a temperature rise due to the heat of reaction leads to a "thermal" explosion. These results are in agreement with the earlier findings that methane, when added in small amounts to hydrogen-oxygen mixtures, does not change the explosion limits, whereas ethane does. The differences between the two hydrocarbons are explained in terms of the different reactivities of the ethyl and methyl radicals.

Cusin and James (Ref. 21, 22 and 23) have studied the inhibition of CO oxidation by cyanogen and by ethane. They also used the static bulb technique. In both cases the inhibition was attributed to removal of oxygen atoms by the inhibitor.

$$c_2 N_2 + 0 \longrightarrow NCO + CN$$
 $c_2 H_6 + 0 \longrightarrow c_2 H_5 + OH$ 

As discussed in our earlier review, the flame speed of very pure  $\text{CO-O}_2$  mixtures is almost zero, and increases markedly with small additions of hydrogen, water or hydrocarbons. These additives apparently supply additional radicals to propagate the reaction, and it is not clear why the hydrocarbons inhibit rather than catalyze explosions. As the authors point out, the reason undoubtedly involves absorption and reaction of the additives on the vessel walls as well as homogeneous reactions. Along these lines, Lewis and von Elbe (Ref. 48) explain why the explosion limits of moist and dry  $\text{CO-O}_2$  mixtures are nearly the same in static vessels, while the flame speeds are different.

In our laboratory (Ref. 71) we have measured flame speeds for the three-component systems hydrogen-air-methane and hydrogen-air-ethylene at low hydrocarbon concentrations. The hydrocarbons are most effective as inhibitors in rich flames.

## 3.2 Inhibition by Halogen-Containing Compounds

Several studies on the inhibiting effects of halogenated hydrocarbons have appeared during the past year, but none have completely defined the inhibition mechanism of these important agents.

The extensive screening studies of Lask and Wagner, mentioned in our earlier report, have now been published in full detail (Ref. 47). They compared many inhibitors on the basis of the amount of inhibitor needed to reduce the flame speed of a hexane-air flame by 30%. Abrams (Ref. 1) used a different approach in measuring the inhibiting effects of methyl bromide and methyl iodide on  $H_2$ -air and  $CH_{\perp}$ -air flames. He established standard uninhibited premixed flames, then measured the amount of inhibitor needed to make the flame blow off the burner. In all cases, methyl iodide was a slightly better inhibitor than the bromide, as would be expected from earlier work. Also, both inhibitors seemed more effective in lean than in rich flames. This latter conclusion, however, is not definite since the amount of inhibitor needed to make the flame blow off depends on the relative stabilities of the standard flames, and these were not necessarily the same at the various equivalence ratios.

Creitz (Ref. 20) has reported on the inhibition of diffusion flames by methyl bromide and trifluoromethyl bromide applied to either the fuel (CO,  $\rm H_2$ ,  $\rm C_2H_6$ ,  $\rm C_3H_8$ ,  $\rm C_4H_{10}$  and  $\rm CH_4$ ) or oxidizer (air or  $\rm O_2$ -enriched air) side of the flame. The inhibitors were much more effective when added to the oxidizer side. This is in agreement with earlier results by Simmons and Wolfhard (Ref. 69), who explained that the several volumes of air needed to react with one volume of fuel contained about the same total amount of inhibitor as the one volume of fuel. Perhaps their explanation could be tested by comparing the results for pure fuel burning in air to those for nitrogen-diluted fuel burning in oxygen.

Van Tiggelen and co-workers (Ref. 79, 80) have continued their systematic studies of the flame speeds of hydrocarbon systems. They report flame speeds for the  $\text{CH}_{4}$ -  $\text{CH}_{3}\text{Cl}-\text{O}_{2}-\text{N}_{2}$  and  $\text{CH}_{4}-\text{CH}_{3}\text{Br}-\text{O}_{2}-\text{N}_{2}$  systems. As would be expected, the  $\text{CH}_{3}\text{Br}$  reduced the flame speeds more strongly than  $\text{CH}_{3}\text{Cl}$ . The results are correlated to give activation energies for flame propagation process. They have also measured OH, CH and  $\text{C}_{2}$  emission intensities from these flames.

Halogenated hydrocarbons are not effective against all types of fires. Markels and co-workers (Ref. 57, 58) found bromotrifluoromethane ineffective against both liquid hydrogen and hydrazine pan fires. Chlorobromomethane was also ineffective against hydrazine and unsym.-dimethylhydrazine. Trichlorotrifluoroethane was effective, apparently more by cooling and blanketing action than by chemical inhibition.

The result for hydrogen fires is in contrast with our studies (Ref. 71) in which bromotrifluoromethane was effective in reducing the flame speed of premixed hydrogen-air flames. The differences between results in the two laboratories are no doubt due to the differences in experimental conditions, and illustrate the need to correlate the various methods of evaluating inhibitors.

Broido (Ref. 14) found that carbon tetrachloride and bromochloromethane actually accelerate the combustion of sugar, apparently by catalyzing the decomposition of the sugar. Several solids normally considered inhibitors, such as potassium bicarbonate and borax, had a similar effect.

R. M. Fristrom and co-workers (Ref. 36, 37) are continuing fundamental studies of the inhibition of low-pressure  $\mathrm{CH_{4}-O_{2}}$  flames by HBr. They are attempting to obtain by the quartz probe not only complete profiles of all the molecules present in the flame, but also radical concentrations. So far developing methods of collecting and analyzing for the radicals has been emphasized with considerable success. When completed, these studies will help greatly in establishing inhibition mechanisms.

An experiment by F. P. Fehlner (Ref. 31) aimed at studying the reaction of chlorine atoms in a flame is interesting more for the method used than for the results (which were inconclusive). He established a low-pressure acetylene-oxygen-chlorine flame, then decomposed the chlorine entering the flame by a flash of light. For a few milliseconds after the flash, the flame front enlarged considerably, indicating inhibition. The technique of combining flash photolysis with flame speed studies was ingenious, although Fehlner felt that a steady source of atoms, such as might be produced by a low pressure discharge, would have been more satisfactory.

## 3.3 \_\_Inhibition by Finely Divided Solids

Studies on the inhibiting effects of solids have extended our factual knowledge without greatly increasing our understanding of their mode of action. Friedrich extended earlier studies of the action of salts to studies of solutions (5-10% salt in water) of K2CO3 KHCO3, Na<sub>2</sub>CO<sub>3</sub>, and NaHCO<sub>3</sub> on solvent fires (Ref. 35). The extinguishing action of the solutions was markedly greater than that of pure water, K2CO3 causing the greatest improvement and NaHCO $_{\text{\tiny Q}}$  the least. This is the order to be expected from previous work. He determined the corrosive properties, electrical conductivity, and freezing point of the solutions, all of which would be important if the salt solutions are used for fire fighting. Rather similar results were reported by Abrams (Ref. 1), who added Na<sub>2</sub>CO<sub>3</sub> and  $K_2$ CO<sub>3</sub> solutions to premixed hydrogen-air and methane-air flames. Though the salts were added in solution, it is likely that the water evaporated and finely divided salts inhibited the flames.

In an attempt to determine the mechanism of inhibition by salts, Friedman and Levy (Ref. 33) added sodium vapor to the methane side of a preheated methane-air diffusion flame. They found, however, that no noticeable change occurred with up to 0.26 atom percent sodium in the methane. We obtained similar negative results on adding sodium vapor to a preheated hydrogen-air diffusion flame (Ref. 72).

Sodium and potassium bicarbonates are effective against hydrazine burning in air (Ref. 57) but not against liquid hydrogen unless applied at very high rates which are impractical except for small fires (Ref. 58). However, if the intensity of the fire is first reduced by the application of foam, then more moderate amounts of these salts extinguish hydrogen fires.

A special-purpose powder extinguisher, useful against metal alkyl fires, contains absorbents such as bentonite and silica gel which aid extinguishment by absorbing the flammable liquid (Ref. 39).

The large scale use of sodium calcium borate slurries to combat forest fires has been described recently (Ref. 4). Millions of gallons have been dropped on fires by aerial tankers, which can rapidly reach otherwise inaccessible regions. The slurry sticks to flammable material, excluding air, reflecting heat, and chemically inhibiting combustion.

## 3.4 Miscellaneous Inhibition Effects

Flash photolysis has been used to study the effects of additives such as tetraethyllead, iron pentacarbonyl and ferrocene, which are engine antiknock agents, on the ignition of fuel-oxygen mixtures at low pressures (Ref. 16, 29, 30). Induction times for ignition, and absorption and emission spectra of the reacting gas have been measured, but the results have been difficult to interpret.

## 4. PHYSICAL METHODS OF FIRE EXTINGUISHMENT

## 4.1 Water Sprays

Only three reports on fire extinguishment with plain water, without additives, were found. This is partly due, no doubt, to the fact that fairly effective methods of handling water have already been worked out. Still, much remains to be learned about the effect of spray properties on extinguishment efficiency.

In many fires, the rate of combustion depends on heat transfer from the flame to the fuel, causing the latter to decompose or evaporate. Water sprays can cool the flame or fuel by direct contact, and also reduce radiant heat transfer from flame to fuel. Sprays are generally more effective than dense streams for these applications, if they can be applied to the zones where they are needed. Rasbach has published a general article on the use of water sprays on many types of fire (Ref. 67).

In a study of the extinguishment of liquid pan fires by water sprays, Rasbach (Ref. 66) obtained quite complex results. For a number of low-boiling liquids, extinguishing efficiency increased markedly as the average droplet diameter decreased from about 0.5 to 0.3 mm, but this was not true of higher-boiling liquids such as transformer oil. Particularly with the low-boiling liquids, and larger drop size, there was a tendency for a flat, difficultly extinguishable flame to be established quite near the liquid surface. One reason these flat flames were hard to extinguish is that the heat release per unit of time and volume in them was several times that in the freely burning flames.

Practical tests on the reduction of radiant heat transfer between structures by water sprays are described by Moran (Ref. 62). It was concluded that much less water is needed to protect a threatened structure by this method than by wetting it down by water streams.

A method of producing large quantities of droplets in the range of 0.1 mm was sought by Malcolm (Ref. 56). No satisfactory way of producing this fine a spray by water pressure alone could be devised, but a combined air-water nozzle could produce sprays containing equal weights of droplets and air. As would be expected with such small drops, the carrying power was low.

As mentioned in Section 3.3, water to which inhibiting salts have been added is considerably more effective than plain water, but rather large amounts of salts must be used. In another approach (Ref. 38), additives to increase the viscosity of the water are added, with the result that the water drains more slowly from the structure. Many practical tests have shown that extinguishment can be accomplished with considerably less water when these additives are used.

## 4.2 Foams

Foams were found to be effective, within limitations, against hydrazine and liquid hydrogen fires (Ref. 57, 58). Hydrazine tended to cause collapse of the foam because of its alkaline chemical action, but foams developed to fight alcohol fires proved sufficiently stable. Foams did not completely extinguish liquid hydrogen fires, but did reduce the intensity of the fires to the point where extinguishment by dry powders could be accomplished easily.

Powders also have a tendency to collapse foam, being usually of an alkaline nature. However, several powder compositions compatible with foam have been formulated (Ref. 74, 76), and a standard method for testing compatibility has been devised (Ref. 45).

A recent development in England has been the use of a jet engine to rapidly generate large quantities of highly expanded detergent foam (Ref. 8). The output of the foam generator is so large that it could fill a large building in a few minutes.

Several references, particularly to patents, describe firefighting foams (Ref. 17, 25, 41, 59, 61, 63, 65). Although a detailed discussion of these lies outside the scope of this review, a study by Jablonski (Ref. 46) on the effect of temperature and air pressure on foam properties deserves mention. He found that better quality foams, from the point of view of stability and drainage rate, could be prepared from cool, rather than warm water, and that quality increased with increasing air pressure up to about 50 psi. These studies relating foam properties to the method of preparation are continuing.

## 5. FIRE-FIGHTING SYSTEMS

# 5.1 Rapid Detection and Extinguishment Systems

Two rapid-acting fire extinguishing systems and a number of fast-response detectors have been recently announced. The systems have so far been applied to ground installations, but could be used, with modifications, in flight vehicles.

One system employs either pressure-sensitive or radiation-sensitive detector, the output of which is amplified and used to open a valve to release extinguishing agent, and also perform other protective functions such as turning off equipment, venting a closed space, or isolating the part of the system which is on fire. The response time of the system, from the time the pressure or light exceeds the threshold sensitivity of the detector until the time extinguishing agent first reaches the fire, is in the range of 20 to 100 milliseconds. In an industrial installation (Ref. 40) the system has proved successful in suppressing explosions in their early stages, preventing serious damage.

The other system (Ref. 6) utilizes an infrared cell as the detector, triggering an explosively actuated valve to release water into a high-capacity sprinkler system. This system can also perform auxiliary functions such as turning off equipment and sounding alarms.

Three flame detectors, using reflection of sound (Ref. 5), ultraviolet radiation (Ref. 43), and infrared

radiation (Ref. 7) were reported. The last system included the use of glass fiber bundles which are flexible and can transmit light from one end to the other. Several of these flexible light transmitters can be used to monitor various positions, including difficultly accessible ones, from a central control station.

An atmospheric monitoring system, capable of detecting parts per million of propellants such as  $F_2$ ,  $B_5H_9$ ,  $N_2H_4$ ,  $NO_2$  and  $ClF_3$  has been described by Ball (Ref. 10). In it, the propellants react with other chemicals to produce finely divided aerosols which are detected by an ionization type analyzer. This instrument can give warning of potentially hazardous propellant build-ups before a fire actually starts.

# 5.2 Fire Protection and Flight Vehicle Reliability

Two planning reports, sponsored by ASD (Ref. 13 and 18) deal with an evaluation of the fire hazards liable to be encountered in space vehicles, and methods of handling them. Hazards associated with the various flight vehicle components are reviewed, and rational methods of deciding what type and how much fire protection to use are presented.

## 6. REVIEW ARTICLES

The report of the NAS-NRC study group (Ref. 64) reviews many aspects of current fire research, such as modern fire-fighting methods, economic aspects, and current understanding of fire propagation in various media. The diverse backgrounds of the participating experts make this a well-rounded integrated study.

A review of chemical fire extinguishing agents was given at the American Chemical Society Symposium on Fire Control Research by Friedman (Ref. 34), and while a broader review, covering all aspects of fire research was given by Berl (Ref. 12). About the same time, our review (Ref. 70) on chemical aspects of fire extinguishment appeared. Rasbach's paper on extinguishment by water sprays, also presented at the A.C.S. Symposium (Ref. 67), is a comprehensive review.

A series of articles dealing with fire protection in chemical and petroleum plants holds value for those concerned with missile bases. The articles (Ref. 68, 81, and 84) cover such topics as explosion limits, ignition sources, flame arrestors, plant layout, and automatic and manual fire-fighting systems.

Of four other review articles on fire protection, one covers the physical and chemical properties of propellants which are important for fire and explosion protection (Ref. 77), one reviews the principles of explosion prevention (Ref. 15), one reviews recent advances in water additives, particularly as they apply to fighting forest fires (Ref. 26), and the last deals with the use of fire retardants in plastics (Ref. 24).

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